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SYNERGISTIC EFFECTS OF MARBLE POWDER ON MECHANICAL PROPERTIES IN 3D PRINTED PLA/PCL HYBRID COMPOSITES

SINERGIJSKI UČINKI MARMORNEGA PRAHU NA MEHANSKE LASTNOSTI 3D TISKANIH PLA/PLC HIBRIDNIH KOMPOZITOV

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Rising concerns about environmental pollution and the depletion of fossil-based resources have increased the demand for biodegradable alternatives to traditional petroleum-based plastics, particularly in industries such as automotive manufacturing. In this study, biodegradable composites made from polylactic acid (PLA) and polycaprolactone (PCL), reinforced with marble powder (MP) as the filler, were developed and thoroughly evaluated. Composite samples were fabricated using 3D printing to ensure precision and consistency. The structural and mechanical properties of the PLA/PCL/MP composites were examined using X-ray diffraction (XRD), Fourier-transform infrared spectroscopy (FTIR), and scanning electron microscopy (SEM). XRD results indicated that the addition of marble powder enhanced the crystallinity of the composites, while FTIR analysis showed chemical interactions between the polymers and the filler, suggesting improved compatibility. SEM images revealed better interfacial bonding and a uniform phase distribution, which contributed to enhanced mechanical performance. Compared to pure PLA/PCL blends, the composites reinforced with marble powder demonstrated significant improvements in tensile strength, flexural strength, impact resistance, and overall density. These results highlight marble powder's dual role as an economical filler and an effective reinforcement. Overall, the findings suggest that PLA/PCL/MP composites are lightweight, durable, and sustainable, making them highly promising for automotive applications as they support the broader move toward eco-friendly, high-performance materials in engineering.

Keywords: polylactic acid, polycaprolactone, marble powder, 3D printing

Naraščajoča zaskrbljenost zaradi onesnaževanja okolja in izčrpavanje virov na osnovi fosilnih goriv je povečala povpraševanje po biorazgradljivih alternativah tradicionalni plastiki na osnovi nafte, zlasti v panogah, kot je avtomobilska industrija. V tem članku avtorji opisujejo študijo razvoja, izdelave in ovrednotenja biorazgradljivih kompozitov iz polilaktida oziroma polilaktične kisline (PLA; angl.: polylactic acid) in polikaprolaktona (PCL; angl.: polycaprolactone), ojačanega z marmornim prahom (MP). Vzorce kompozitov so avtorji izdelali s tehniko 3D tiskanja, ki zagotavlja dobro natančnost in konsistenco. Na izdelanih preizkušancih iz PLA/PCL/MP kompozitov so določili strukturne in mehanske lastnosti. Za to so uporabili spektroskopijo na osnovi sipanja rentgenskih žarkov (XRD; angl.: X-ray diffraction), Fourierjevo transformacijsko infrardečo spektroskopijo (FTIR; angl.: Fourier-transform infrared spectroscopy), vrstično elektronsko mikroskopijo (SEM; angl.: scanning electron microscopy) in izvedli mehanske preiskuse. Rezultati XRD spektroskopije so pokazali, da dodani marmorni prah izboljša kristaliničnost kompozita, medtem ko je FTIR analiza nakazala na kemične reakcije med polimeroma in polnilom. SEM posnetki so odkrili izboljšanje kohezije na faznih mejah in njihovo enovito porazdelitev, kar prispeva k izboljšanju mehanskih lastnosti. Primerjava med čistimi PLA/PCL mešanicami in z marmornim prahom ojačanimi kompoziti je pokazala, da imajo slednji pomembno izboljšano natezno in upogibno trdnost, žilavost (odpornost proti udarcem) ter celokupno gostoto. Rezultati te raziskave so pokazali dvojno učinkovitost dodanega marmornega prahu; to je: kot ekonomično polnilo in kot učinkovito sredstvo za ojačitev (armiranje). Na splošno ugotovitve kažejo, da so kompoziti PLA/PCL/MP lahki, trpežni in trajnostni, zaradi česar so zelo obetavni materiali za avtomobilsko industrijo in podpirajo obsežnejši prehod na okolju prijazne, visokozmogljive inženirske materiale.

Ključne besede: polilaktatna kislina, polikaprolakton, marmornati prah, 3D tiskanje

1 INTRODUCTION

The need for enhanced fuel efficiency, reduced emissions, and improved performance is driving a significant transformation in the automotive industry. Increasing the use of materials that are lightweight, especially polymers, which have several benefits over conventional materials such as metals and glass, is an important component of this change. By reducing the overall weight of vehicles, manufacturers can achieve better fuel economy, which is essential in meeting stringent regulatory standards and consumer demands for greener vehicles. A weight reduction of just 10 % can lead to an improvement in fuel efficiency of approximately 6–8 %. Reduced weight can enhance acceleration, braking, and handling characteristics, leading to improved driving dynamics. As industries advance, the use of high-performance polymer composites – especially those enhanced with innovative fillers like marble powder – is becoming increasingly important in modern automotive engineering. Environmentally friendly plastics and recyclable materials are attracting attention not only for their

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sustainability but also for their biocompatibility. This characteristic allows such polymers to be safely used in the human body, where they can be absorbed or broken down without causing harm. As a result, these materials find applications in the medical field, supporting tissue regeneration, assisting in the healing of injuries, and reducing recovery times.

Commonly used polymers for these purposes include poly(3-hydroxybutyrate), polylactic acid (PLA), polyglycolic acid (PGA), and polycaprolactone (PCL), along with their blends and copolymers.[1] Modern industries like packaging and textiles widely use PLA, and it is increasingly becoming useful in bioengineering for reusable items. Because of its gentler impact on the environment, PLA provides substantial benefits in this area. PLA helps reduce reliance on fossil fuels and lowers environmental impact, as it is a biodegradable polymer derived from natural sources like sugarcane or corn starch. Its ability to be recycled further supports sustainability by minimizing plastic waste and promoting a circular economy. Additionally, PLA is an excellent material for many uses due to its low toxicity, ease of fabrication, and excellent strength in mechanical applications. Several uses have revealed the advantages of this material, which include little to no documented hazardous effects, biodegradability, biocompatibility, recyclability, easy manufacturing, and environmental friendliness.[2] For instance, the inclusion of jute fibre in PLA significantly enhances tensile strength and modulus[3], while toughened PLA formulations improve flexural strength and impact resistance.[4] Similarly, the inclusion of fillers like aluminium oxide (Al_2O_3) improves the flexural modulus and overall mechanical characteristics of PLA composites, allowing their use in engineering applications.[5] Numerous studies on the mechanical features of PLA/PCL combinations have shown that by adding or modifying certain components, these materials may be significantly improved. These combinations are ideal for uses such as packaging and tissue engineering due to their biodegradability, ductility, and strength. Investigators discovered that adding PCL to a PLA matrix significantly increased toughness.[6] An addition of dimethyl sulfone (DMSO2) to PLA/PCL composites improves their yield strength and modulus, enhancing the overall mechanical performance.[7]

Additionally, reactive compatibilisation of PLA with PCL improves impact resistance and elongation at break.[8] A blend of PLA/PCL with bamboo charcoal further demonstrates excellent mechanical properties, combining high tensile strength with superior elongation at break. [9] These results underscore the versatility of PLA/PCL composites, demonstrating their ability to deliver enhanced mechanical performance while remaining biodegradable and environmentally friendly. PLA, in particular, is a biodegradable polymer that can break down into harmless substances like carbon dioxide and water under suitable conditions. Being a thermoplastic, it can be processed similarly to traditional synthetic plastics through methods like injection moulding, thermoforming, blow moulding, and extrusion.[10] PCL is not inherently bioactive and degrades relatively quickly. Its degradation rate and properties can be modified by changing its molecular weight or crystalline structure, or by incorporating hydrophilic additives such as polyethylene glycol or ceramic materials. Furthermore, copolymerization with PLA is another option. The combination of PLA and PCL has several advantages in the food packaging industry, including good strength, resistance to UV radiation, and thermal resistance.[11,12] Several research efforts have concentrated on aliphatic polyesters, such as PLA and PCL, as the most significant biodegradable materials.[13] It has been estimated that the total manufacture of polymers worldwide has reached nearly nine billion tons.[14] Toughening agents or polymers might be used to increase the hardness of the PLA matrix. Furthermore, PCL has favourable mechanical qualities that aid in the scaffold's structural stability over long durations.[15,16] Combining PLA with other polymers offers a more feasible and economical method for improving its toughness.[17,18]

The production of marble generates both liquid and solid waste. Due to the significant accumulation of marble waste, there is an increasing focus on effectively managing these waste materials.[19] Using marble powder helps divert waste from the marble industry that would otherwise end up in landfills. While green composites may soon be able to replace synthetic polymeric materials, they are already used in areas such as medical applications, agricultural products, and automobile components.[20] Andrew and Dhakal (2022)[21] pointed out that recent developments in waste management had provided an approach for the preparation of a significant quantity of viable composite materials. According to another research[22], the utilization of nanofiller mixtures significantly improved the rigid modulus of a PLA/PCL matrix, demonstrating substantial co-reinforcement compared to filling the nanofillers individually. The combined use of quartz sand and marble sludge powder proved highly effective due to their complementary micro-filling properties and pozzolanic activity. A study reported a 28 % increase in flexural modulus with an MP addition, reinforcing its effectiveness.[23] Dhanalakshmi et al. offer clear recommendations for incorporating marble powder in the concrete production.[24]

The integration of marble powder in automotive applications addresses performance requirements and also brings it into line with broader goals of sustainability, waste reduction, and reduced carbon emissions. Marble-PLA, also known as marble-infused PLA, is a composite material formed by incorporating marble particles into a PLA matrix. This combination boosts biodegradability and replicates the aesthetic qualities of natural marble. As a result, marble-PLA has become more popular for various applications, including decorative items,

Table 1: Description of materials and their properties[26–28]

Material	Polylactic Acid (PLA)	Polycaprolactone (PCL)	Marble powder (MP)
Monomer	Lactic acid ($C_3H_6O_3$)	ε-Caprolactone ($C_6H_{10}O_2$)	Calcium carbonate ($CaCO_3$)
Structure	Semi-crystalline	Semi-crystalline	Crystalline mineral form
Density (g/cm³)	1.32	1.07	2.70
Melting point (°C)	150–160	60–65	750–825
Thermal stability	Moderate	Low	High
Mechanical stability	Moderate	Low	High
Biodegradability	Biodegradable	Biodegradable	Non-biodegradable

architectural models, artistic sculptures, and custom home decor. However, there is limited research on its performance and mechanical properties, underscoring the necessity for further study and exploration in this field.[25]

2 EXPERIMENTAL PART

2.1 Materials used

See **Table 1**.

2.3 Characterisation of specimens

2.3.1 X-ray diffraction analysis

The X-ray diffraction (XRD) analysis was performed using a BRUKER D8 ECO ADVANCE diffractometer equipped with a Cu Kα radiation source λ in nm. The measurements were conducted in the TwoTheta/Theta scanning mode over a 2θ range of 10–80°, with a step interval of 0.02°, utilising a LynxEye detector. All tests were carried out at ambient conditions, at approximately 25 °C.

2.3.2 FTIR analysis

FTIR was performed using a Shimadzu IR Tracer-100 spectrometer, which features a high resolution of 0.25 cm^{-1}. The instrument is equipped with high-speed scanning capabilities, enabling the acquisition of up to 20 spectra per second. Tests were conducted in either transmission or attenuated total reflectance (ATR) mode, utilising enhanced dynamic alignment, and an interferometer equipped with a dehumidifier, acquiring over 12,000 spectra. The information analysis program included features for detecting contaminants, monitoring responses, and evaluating time-dependent changes.

2.3.3 Solid density analysis

To evaluate the solid density of PLA, PCL, and their composites containing nanoparticles like marble powder, one can rely on the basic principles such as the rule of mixtures alongside experimental measurements. Solid density is determined by measuring the mass of a material relative to its volume, usually expressed in g/cm³, following ASTM D 256 standards.

2.4 Mechanical properties

2.4.1 Flexural test of composites

A Tinus Olsen H10KL universal testing machine (UTM), designed for flexural testing, was utilised. It has a maximum load capacity of 10 kN. The flexural test was conducted in accordance with ASTM D790, using a 60 mm gauge length, a crosshead speed of 1 mm/min, and specimens with dimensions of (125 × 12.7 × 3.75) mm. The average print time required to print each flexural test specimen was approximately 30 minutes under the specified conditions.

2.4.1 Impact test of composites

Impact tests were carried out using the Tinus Olsen IT 503 UTM in accordance with ASTM D256 standards. This machine, with a loading capacity ranging from 0.5 to 50 kN, was used to evaluate the impact resistance of the materials. The average print time required to fabricate each impact test specimen was approximately 15 minutes under the specified conditions.

2.4.2 Tensile strength of composites

Tensile tests, conducted in accordance with ASTM D638, were conducted using the Tinus Olsen H10KL UTM. Specimens with dimensions of (250 × 25 × 3) mm were tested, with the machine's maximum load capacity being 10 kN. This advanced testing system, featuring built-in pneumatic distribution ports, ensured a secure operation of the grips. The Tinus Olsen horizon data analysis software provided accurate data acquisition and analysis, facilitating a reliable evaluation of tensile properties. The average print time required to fabricate each tensile test specimen was approximately 42 minutes under the specified conditions.

2.5 SEM analysis

The SEM analysis was conducted using ZEISS EVO 18 from Carl Zeiss, Germany, which was designed for high-resolution imaging and analysis. It features a tungsten filament and provides a secondary electron image resolution of 50 nm, depending on the sample. The microscope includes a BSD detector and offers a tilt range of 0–60°.

3 RESULTS AND DISCUSSION

3.1 XRD characterisation

The XRD pattern of pure PLA shows a broad, weak hump, typical of an amorphous material. This amorphous nature arises from PLA's rigid molecular chains, which restrict their movement and hinder the formation of an ordered crystalline structure. The lack of sharp diffraction peaks confirms that most of the PLA remains in the amorphous phase. Such a structure is beneficial for applications requiring transparency and flexibility; however, lower crystallinity may limit its mechanical strength and thermal stability. XRD analysis of polymer composites thus provides valuable information about their crystallinity and how composition affects material properties.

In contrast, pure PCL exhibits sharp, well-defined peaks at around 2θ = 21.4° and 28.5°, reflecting its semi-crystalline nature. The flexible molecular chains of PCL promote better chain alignment and crystal formation, resulting in highly ordered crystalline regions. This semi-crystalline structure enhances PCL's mechanical performance, giving it superior toughness and flexibility – qualities that make it suitable for durable and resilient applications. The clear peaks also suggest that PCL crystallizes readily under normal processing conditions, unlike PLA, which often requires specific conditions or nucleating agents to improve its crystallinity.

The XRD pattern of the 80 % PLA–20 % PCL blend shows broader and less intense peaks compared to pure PCL, indicating a moderate degree of crystallinity. This reduction in crystallinity is due to the partial miscibility and interaction between PLA and PCL phases, which disrupt the ordered packing of chains and lower the overall crystal formation. Blending PCL with the PLA matrix leads to the formation of crystalline regions; however, the amorphous nature of PLA interferes with the orderly arrangement of PCL chains, preventing complete crystallization. In comparison, pure PCL shows sharp and well-defined peaks at 2θ values of 21.4° and 28.5°, confirming its semi-crystalline structure. The resulting PLA–PCL blend thus combines the amorphous behaviour of PLA with the semi-crystalline properties of PCL, creating a material that balances flexibility and structural order. The broader peaks observed in the XRD pattern indicate a higher amorphous content, suggesting a more heterogeneous structure with limited long-range molecular ordering.

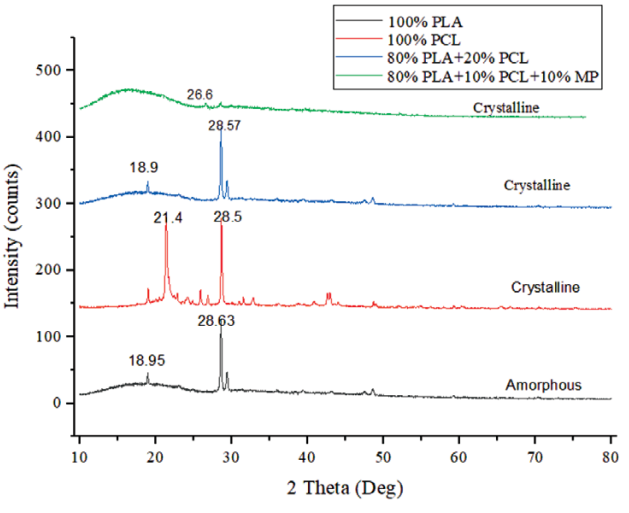

Figure 1: XRD results of the composites

In the 80 % PLA + 10 % PCL + 10 % MP sample, the XRD profile displays broader peaks with an increased baseline intensity. The addition of marble powder (mainly calcium carbonate, $CaCO_3$) acts as a nucleating agent, promoting molecular aggregation within the polymer matrix. However, instead of forming sharp diffraction peaks, the marble powder causes diffuse scattering, indicating that it disrupts polymer crystallinity rather than forming distinct crystalline regions of its own. This scattering likely results from the interactions between the filler particles and the polymer chains. The peak broadening signifies reduced crystallinity, as the filler particles hinder regular chain alignment. Although this reduction may slightly decrease stiffness and thermal stability, it can improve properties like impact resistance and toughness. Overall, the XRD results highlight the intricate relationship between polymer blending and filler incorporation in determining the structural and physical behaviour of the composites. While the high crystallinity of pure PCL enhances flexibility and toughness, the amorphous nature of PLA provides good ductility and ease of processing. However, PLA's limited resistance to weathering makes it less suitable for long-term applications – a limitation that can be mitigated by adding fillers or other reinforcing agents. By blending PLA with PCL, the thermal properties of the composite can be tuned by altering the amorphous to the semi-crystalline phase ratio.[29]

The 80 % PLA + 20 % PCL blend demonstrates a well-balanced structure, reflecting the combined characteristics of both polymers. The greater proportion of amorphous PLA reduces the overall crystallinity, as shown by the broader and weaker XRD peaks compared to pure PCL. This decrease in crystallinity, caused by partial miscibility and phase interaction between PLA and PCL, influences the composite's mechanical behaviour. With a higher amorphous content, the material becomes less thermally stable and more likely to soften at elevated temperatures. Nevertheless, the blend offers better flexibility and easier thermal processing than pure PLA, making it suitable for applications such as packaging, where moderate strength and improved flexibility are important.

In the 80 % PLA + 10 % PCL + 10 % MP composite, the XRD pattern displays an increased baseline intensity along with broader peaks. The inclusion of marble powder, mainly consisting of calcium carbonate ($CaCO_3$),

acts as a nucleating agent while simultaneously disturbing the polymer's crystalline regions, leading to a more disordered structure. The dual role of calcium carbonate[30] is to enhance nucleation while introducing heterogeneity. The diffuse scattering suggests that the filler interacts with the polymer matrix, leading to reduced crystallinity while improving impact resistance and toughness. The XRD pattern also reveals diffuse scattering, indicating that the interaction between the marble powder and the polymer matrix is not fully crystalline. The presence of the filler disturbs the orderly arrangement of the polymer chains, resulting in reduced overall crystallinity. Generally, improved crystal formation enhances the material's mechanical performance, while higher crystallinity tends to increase the composite's strength and structural integrity.

3.2 FTIR spectrum analysis

FTIR analysis identifies key functional groups in polymer composites. 100 % PLA shows a strong C=O stretching peak at 1749 cm^{-1}, confirming ester groups. The absence of peaks in the 3300–3500 cm^{-1} range indicates there is no O-H stretching, ruling out the presence of carboxylic acid or alcohol.

The peaks around 2850–3000 cm^{-1} confirm aliphatic hydrocarbons, typical of polyesters. 100 % PCL exhibits a similar ester peak at 1736 cm^{-1}, confirming its polyester nature. The peaks between 2850–3000 cm^{-1} indicate C-H stretching from aliphatic groups. The 80 % PLA + 20 % PCL blend retains PLA's dominant ester peak, though slightly shifted due to PLA/PCL interaction. The reduction in intensity of the peak between 1670–1760 cm^{-1} indicates possible hydrogen bonding interactions between the C=O groups of PLA and the –OH groups of PCL. In the 80 % PLA + 10 % PCL + 10 % MP composite, new absorption bands appear at 3442 cm^{-1} and 3362 cm^{-1} corresponding to O–H stretching vibrations, which may arise from moisture absorption or the presence of hydroxyl or alcohol groups. The appearance of a peak near 2169 cm^{-1} points to potential triple bond vibrations, while the shifts observed at lower wavenumbers (around 630 cm^{-1} and 470 cm^{-1}) indicate structural changes in the polymer matrix caused by the addition of marble powder. Overall, FTIR confirms that PLA and PCL are polyesters, with the blends showing intermolecular interactions. Marble powder alters the structure, enhancing flexibility and impact resistance. Ainhoa Fernandez and et al. reported that FT-IR spectra of all films show the typical absorption bands of polyesters, including PLA and PCL. The peaks at 2998 and 2949 cm^{-1} are linked to C–H stretching vibrations from methyl, methylene, and methyne groups. The band at 1745 cm^{-1} corresponds to carbonyl (C=O) stretching, while the region between 748 and 1200 cm^{-1} reflects the skeletal vibrations of the polymer backbone.[31]

3.3 Tensile strength of the composites

The tensile properties of the 100 % PLA, 100 % PCL, 80 % PLA + 20 % PCL, and 80 % PLA + 10 % PCL + 10 % MP were studied. The inclusion of marble

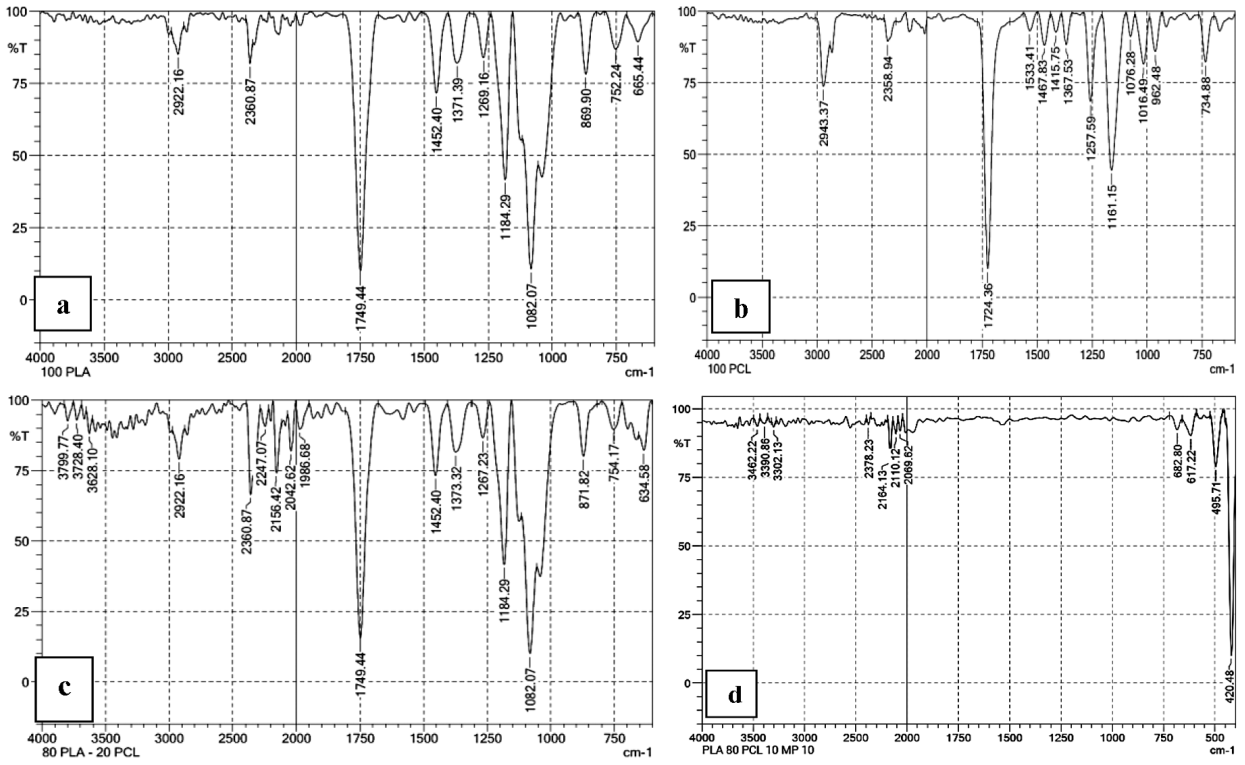

Figure 2: FTIR results for a) 100 % PLA, b) 100 % PCL, c) 80 % PLA + 20 % PCL, d) 80 % PLA + 10 % PCL + 10 % MP

particles plays a vital part in the improved mechanical behaviour of the polymer matrix. The PLA has a higher tensile strength than PCL. To improve the flexibility of a material, a minimum amount of PCL must be added to achieve the desired tensile properties. The difference between the tensile strength of 100 % PLA and 80 % PLA 20 % PCL is 7.1 MPa, and the percentage difference is 26.9 %. For 100 % PCL and 80 % PLA + 20 % PCL, the respective differences are 22.59 MPa and an 85.5 %. 100 % PLA shows a lower ultimate force compared to the mixed materials, indicating that although it has decent properties, it may not perform as well under stress as composite materials. PLA 80 % + PCL 20 % and PLA 80 % + PCL 10 % + MP 10 % blends exhibit significantly higher forces and ultimate stresses, suggesting that the inclusion of PCL and marble powder enhances mechanical properties, possibly through improved toughness and stress distribution. B.T. Duymaz et al. (2019)[32] found that inorganic fillers larger than 100 nm reduce composite strength. The tensile strengths of different compositions of PLA, PCL, and their composites show how tensile properties vary with material composition. 100 % PLA exhibits a tensile strength of 19.3 MPa, which is relatively high owing to its crystalline structure that provides rigidity and strength. However, PLA's brittleness limits its mechanical performance in applications requiring flexibility. In contrast, 100 % PCL has a tensile strength of 3.81 MPa. Known for its ductility and flexibility, PCL lacks the structural rigidity necessary for high tensile strength, largely due to its low crystallinity and flexible molecular structure. The blend of 80 % PLA and 20 % PCL achieves a tensile strength of 26.4 MPa, higher than those of 100 % PLA or 100 % PCL alone. By combining these two polymers, the blend benefits from the rigidity of PLA while gaining some flexibility from PCL. Even though PLA and PCL cannot be mixed, the partial dispersion of PCL within the PLA matrix helps distribute stress more effectively, improving resistance to deformation. However, the tensile strength augmentation is restricted because of the absence of significant interfacial interaction between PLA and PCL.

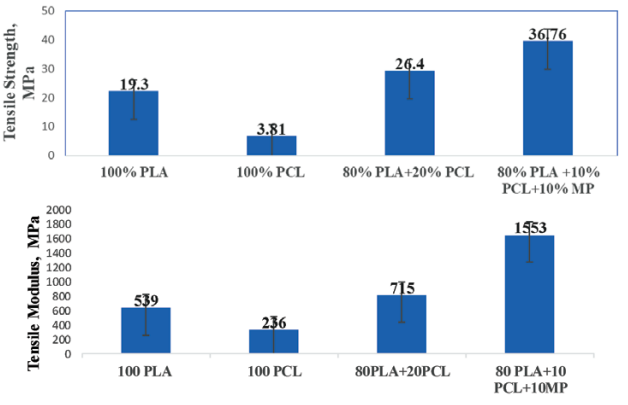

Figure 3: Tensile strength and modulus of the composites

The composite of 80 % PLA, 10 % PCL, and 10 % marble powder exhibits the highest tensile strength of 36.76 MPa. The addition of MP, a rigid inorganic filler, significantly strengthens the PLA/PCL blend by reinforcing the polymer matrix and distributing stress more effectively. MP particles also act as barriers to crack propagation, which further improves the tensile strength. Moreover, the addition of marble powder strengthens the interface between the filler and the PLA/PCL matrix, improving stress transfer and resulting in higher tensile strength. This improvement is largely due to the formation of rigid surfaces within the polymer matrix caused by the incorporation of marble powder. The variations in tensile strength across these compositions reflect the unique properties and interactions of each component. 100 % PLA and 100 % PCL show moderate and low tensile strengths due to their inherent characteristics, while the 80 % PLA + 20 % PCL mix shows an intermediate increase in strength. The most significant improvement is observed in the PLA/PCL/MP composite, where MP acts as an effective reinforcing agent, enhancing the material's ability to withstand tensile loads due to the increase in the tensile strength of the PLA-PCL mix. Added marble powder causes several synergistic processes that improve the composite's mechanical characteristics. Marble powder, a hard inorganic filler, strengthens the polymer matrix by spreading the applied tensile load more uniformly and lowering stress concentrations. This reinforcing action increases the total load-bearing capability of the composite. The marble particles' excellent interfacial adherence to the PLA-PCL matrix enables effective stress transmission during tensile loading. The interface between the filler and the polymer matrix ensures that applied stress passes from the polymer matrix to the solid additive particles, enhancing the material's tensile strength. Furthermore, marble powder inhibits polymer chain mobility, especially in amorphous areas, increasing stiffness and tensile resistance. Additionally, marble powder functions as a fracture-arresting agent, preventing crack initiation and propagation inside the composite material. The stiff particles form a barrier that causes fractures to deflect or bifurcate, increasing the material's resistance to fracture under tensile pressure. The filler also helps to generate a more crystalline structure in the PLA phase by acting as a nucleating agent.

The enhanced crystallinity increases the composite's tensile strength by forming a denser and more organised structure that resists deformation. The tensile modulus of the composites demonstrates a significant enhancement with the incorporation of both PCL and marble powder (MP) into the PLA matrix. 100 % PLA exhibits a tensile modulus of 539 MPa, whereas 100 % PCL shows a substantially lower modulus of 236 MPa, reflecting the inherently flexible nature of PCL. The PLA/PCL blend (80PLA + 20PCL) shows an intermediate modulus of 715 MPa, indicating partial reinforcement from PLA while benefiting from the ductility of PCL. Notably, the

addition of marble powder to the PLA/PCL blend (80PLA + 10PCL + 10MP) results in a dramatic increase in tensile modulus to 1553 MPa, representing more than a twofold improvement compared to the PLA/PCL blend, and nearly threefold improvement relative to 100 % PLA. This substantial increase highlights the reinforcing effect of MP, which enhances the load transfer efficiency within the composite, likely due to improved crystallinity and refined phase morphology as confirmed by SEM and XRD analyses. These results indicate that MP acts as an effective high-density filler, significantly enhancing the stiffness and mechanical stability of PLA/PCL composites for potential automotive applications.

The SEM images illustrate the tensile fracture surfaces of specimens composed of different material formulations. 100 % PLA displays a rupture surface, characterised by features such as ductile tearing, pitted zones, and round voids. These attributes suggest that PLA undergoes a certain degree of plastic deformation before fracture, indicating moderate toughness. The observed multi-layered structure results from fracture propagation along multiple planes, likely due to the inherent microstructural properties of PLA. The round voids act as stress concentrators, facilitating the initiation and propagation of cracks, ultimately leading to failure. The fracture surface of 100 % PCL exhibits a highly ductile failure mechanism. Smooth regions on the fractured surface indicate significant plastic deformation, demonstrating PCL's flexibility. The presence of microvoids and crack formation suggests that the material underwent elongation before fracturing, with the voids serving as precursors for crack propagation. These features highlight PCL's ability to absorb energy and resist brittle failure. The fracture surface of the 80 % PLA/20 % PCL blend shows a layered structure reflecting the phase separation between the PLA and PCL components. While the addition of PCL enhances ductility compared to 100 % PLA, regions of brittle fracture are still evident, with cracks propagating predominantly through the PLA-rich matrix. The microparticles on the surface likely represent the remnants of polymer layers torn during tensile testing, pointing to the heterogeneous failure behaviour of the blend. The fracture surface of the composite is composed of 80 % PLA, 10 % PCL, and 10 % marble powder. Marble powder appears as distinct particles embedded within the matrix, contributing to increased stiffness. However, gaps around the marble powder particles indicate weak interfacial adhesion to the PLA/PCL matrix. Insufficient bonding creates points of stress concentra-

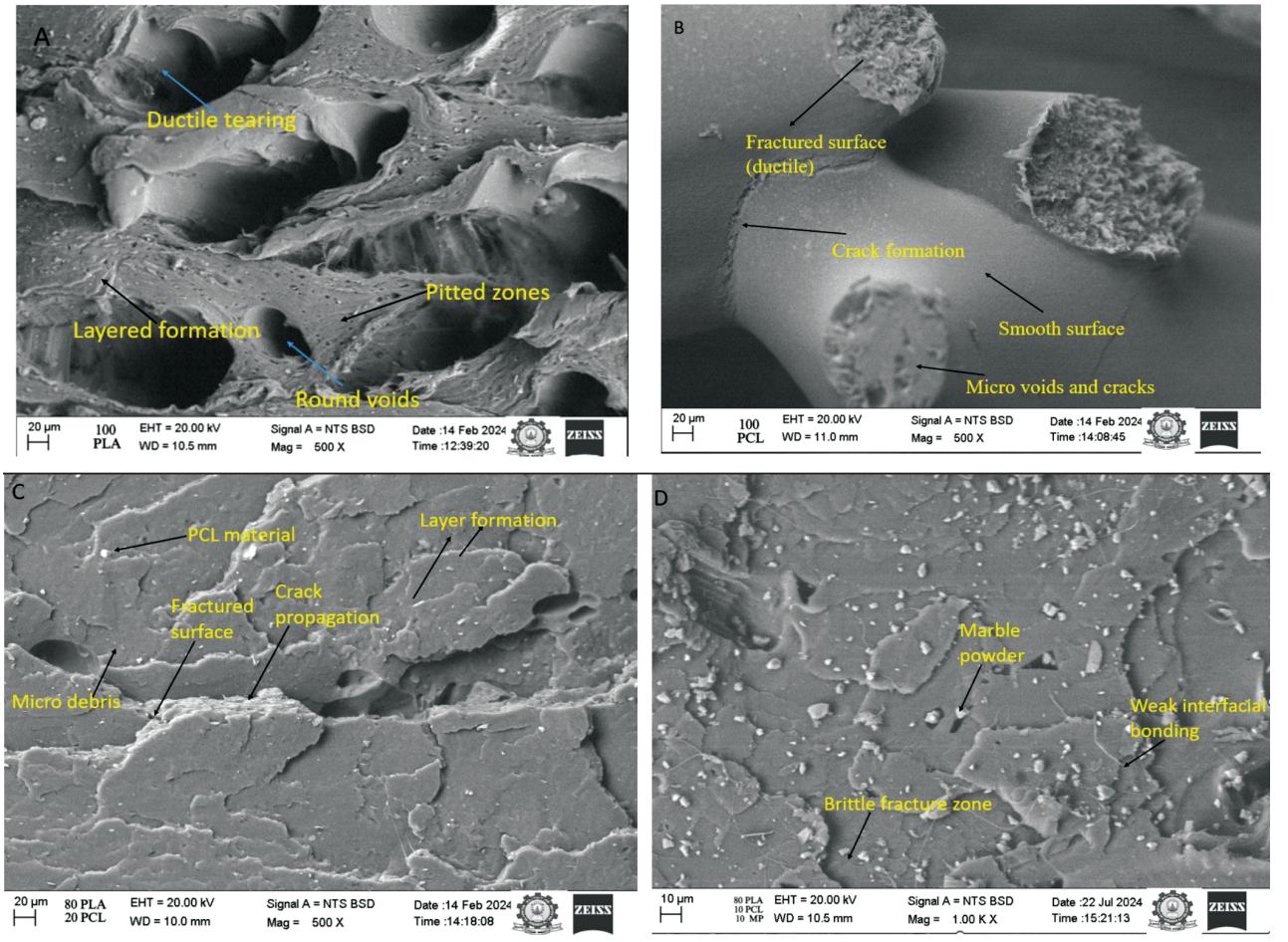

Figure 4: SEM images of tensile-tested specimens

tion, weakening the composite's mechanical integrity and increasing its likelihood of early failure. The brittle fracture regions, primarily observed in the PLA matrix, emphasise the adverse impact of poor filler-polymer adhesion on the overall fracture behaviour. The brittle fracture zones, predominantly observed in the PLA matrix, underscore the negative impact of inadequate filler-polymer bonding on the overall fracture behaviour.

In summary, the SEM analysis highlights the unique fracture features of PLA, PCL, and their composites, both with and without the addition of marble powder. 100 % PLA and the PLA/PCL blend exhibit brittle fracture with moderate ductility, whereas 100 % PCL demonstrates significant plastic deformation. Although marble powder enhances stiffness, its weak interfacial bonding with the matrix introduces stress concentrators, leading to predominantly brittle failure in the composite. These observations provide critical insights into these materials' microstructural and mechanical behaviour.

3.4 Flexural strength of the composites

A comparative flexural strength analysis provides crucial insights into the design of sustainable polymer composites with tailored performance. The poor performance of 100 % PCL (5.17 MPa) compared to that of 100 % PLA (42.31 MPa) confirms the intrinsic material differences: PLA is stiff but brittle, whereas PCL is flexible but mechanically weak under bending loads. However, the marked improvement in the flexural strength observed in the PLA/PCL (80/20) blend (60.03 MPa) demonstrates a clear synergistic effect, where the ductility of PCL counterbalances the brittleness of PLA, resulting in better stress distribution, reduced crack propagation, and higher toughness. This outcome emphasises the importance of polymer blending strategies in overcoming the limitations of individual biopolymers.

The role of marble powder (MP) is particularly significant. Adding 10 % marble powder to the PLA/PCL matrix boosts the flexural strength to 66.85 MPa, showing that MP serves both as an economical filler and a strong reinforcing component. The improvement is likely due to enhanced interfacial bonding between the filler and the polymer matrix, as well as improved load transfer efficiency. Similar reinforcement effects were reported by Pedrazzoli et al. (2014)[23], who noted a 28 % increase in the flexural modulus with an MP incorporation. This result strengthens the argument that mineral fillers, such as MP, can serve a dual role, reinforcing mechanical properties while simultaneously promoting sustainability by valorising industrial by-products.

From a research focus perspective, these findings highlight the potential of multiphase composites (PLA/PCL/MP) as next-generation materials for structural and semi-structural applications. The combination of PLA's stiffness, PCL's flexibility, and MP's reinforcement creates a platform for engineering composites with customizable properties. Such composites can be tailored to meet the demanding mechanical requirements of automotive, packaging, and biomedical sectors, while also addressing environmental concerns through biodegradability and waste utilisation. This research highlights the importance of a systematic approach to optimising blend ratios and filler content, advancing the broader scientific goal of developing high-performance, eco-friendly polymer composites that rival or surpass conventional petroleum-based plastics. The flexural modulus of the investigated materials showed significant variation depending on the composition of PLA, PCL, and MP. 100 % PLA exhibited a modulus of 2410 MPa, consistent with its rigid and brittle nature, while 100 % PCL displayed a much lower modulus of 295 MPa due to its highly ductile and flexible characteristics. The incorporation of 20 % PCL into PLA increased the modulus to 3693 MPa, suggesting that moderate blending improves the stiffness of the matrix, possibly due to partial compatibility and enhanced interfacial interactions between the polymers. Notably, the addition of marble powder further enhanced the mechanical performance, with the 80PLA–10PCL–10MP composite achieving the highest modulus of 6220 MPa. The significant improvement can be attributed to the reinforcing effect of marble powder, which restricts polymer chain mobility and facilitates effective load transfer, thereby increasing the rigidity of the composite. These results indicate that while PCL contributes to toughness, the synergistic effect of the PCL and MP reinforcement markedly improves the stiffness, making PLA/PCL/MP composites suitable for structural and load-bearing applications.

The SEM analysis of flexural fracture surfaces provides critical insights into the failure mechanisms and mechanical behaviour of PLA, PCL, and their composites.

100 % PLA exhibits a fracture surface with sharp edges and river-like patterns, which are characteristic of brittle failure. The absence of plastic deformation and the presence of smooth fractured planes confirm its brittle nature and tendency to fail abruptly under flexural

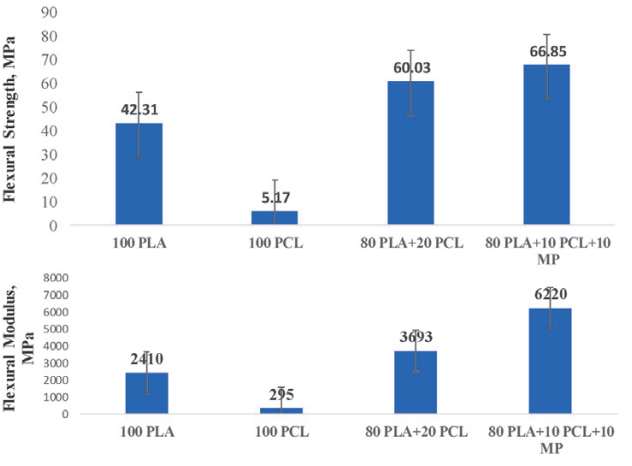

Figure 5: Flexural strength and modulus of the composites

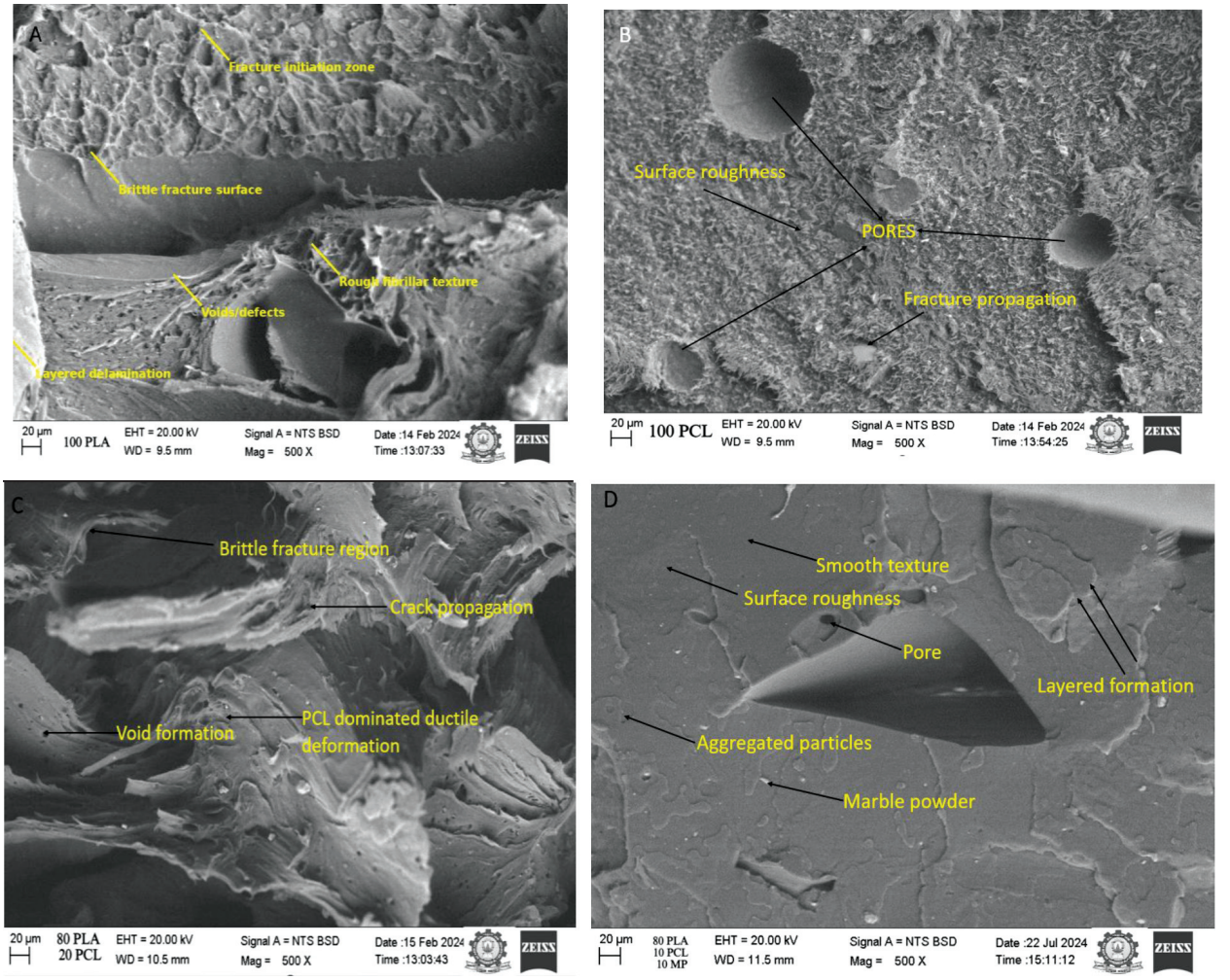

Figure 6: SEM images of flexural test specimens

stress. In contrast, the 80 % PLA/20% PCL blend shows a combination of brittle and ductile regions. The presence of voids indicates phase separation or weak interfacial bonding between PLA and PCL. However, features of plastic deformation and crack propagation suggest improved toughness compared to 100 % PLA, as PCL contributes to energy absorption and delays crack growth. For 100 % PCL, the fracture surface reveals distinct pores, surface roughness, and evidence of fracture propagation. The pores, most likely caused by air entrapment during processing or stress application, act as stress concentrators and reduce structural integrity. The rough texture reflects its ductile nature, where localised elongation and tearing absorb energy during deformation. Fracture propagation lines highlight gradual crack initiation and growth, demonstrating the ductile failure mechanisms of PCL. While it exhibits good toughness, its susceptibility to void formation suggests that processing improvements are necessary to enhance mechanical reliability. The PLA/10% PCL/10% MP composite displays features of both brittle and ductile behaviour. Smooth fractured regions and layered morphologies indicate brittleness, while rougher regions reflect ductility caused by PCL. However, aggregated MP particles and pores act as stress concentrators, strengthening interfacial bonding. Despite these defects, the composite demonstrates a balance between stiffness, toughness, and ductility, with added MP improving toughness and enhancing reinforcement.

In summary, PLA fractures in a brittle manner, PCL fails in a ductile mode, and the blends show intermediate behaviour depending on the composition. The addition of MP improves toughness and increases stiffness, but may introduce defects such as pores and particle clustering. These observations highlight the need to optimise both composition and interfacial bonding to achieve composites with a desirable balance of strength, toughness, and structural integrity.

3.5 Impact strength of composites

The analysis of impact strength across different compositions underscores the importance of synergistic design of polymer composites. 100 % PLA, despite its relatively high crystallinity and stiffness, demonstrates only moderate impact resistance due to its inherent brittleness and limited capacity to dissipate dynamic stresses. On

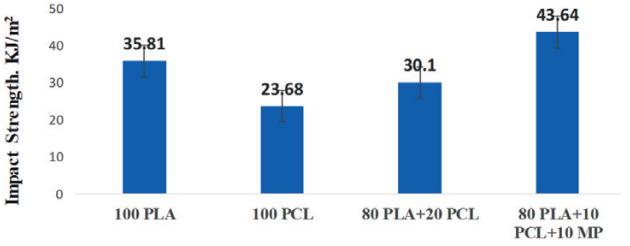

Figure 7: Impact test composites

the other hand, PCL, while ductile and flexible, exhibits a comparatively lower impact strength, as its amorphous and soft structure lacks the rigidity necessary to withstand high-energy loading. These contrasting behaviours highlight the fundamental limitations of neat polymers when used independently.

Blending PLA with 20 % PCL results in an intermediate impact strength, indicating that PCL introduces toughness and flexibility into the brittle PLA matrix. However, the immiscibility of the two polymers restricts efficient stress transfer across the phases, leading to compromised impact performance. This limitation suggests that polymer blending alone is insufficient to achieve optimal toughness and points to the need for additional reinforcement strategies.

The incorporation of marble powder into the PLA/PCL matrix produces the most significant improvement in impact strength, with the 80/10/10 composite exhibiting superior performance compared to all other formulations. MP acts as a reinforcing filler that not only distributes and absorbs impact energy but also serves as a barrier against crack initiation and propagation. Moreover, MP likely modifies the microstructure and enhances interfacial adhesion within the PLA/PCL matrix, facilitating better stress transfer and overall energy absorption under dynamic loading.

These findings demonstrate the potential of MP as a multifunctional additive that overcomes the immiscibility challenges of PLA/PCL blends while simultaneously reinforcing the composite. The ability of MP to enhance impact strength positions it as a sustainable, cost-effective, and performance-enhancing filler for biodegradable composites. This highlights a broader materials design strategy: by carefully selecting both polymer blends and particulate reinforcements, it is possible to blend composites that balance stiffness, toughness, and impact resistance. Such progressions are particularly rel-

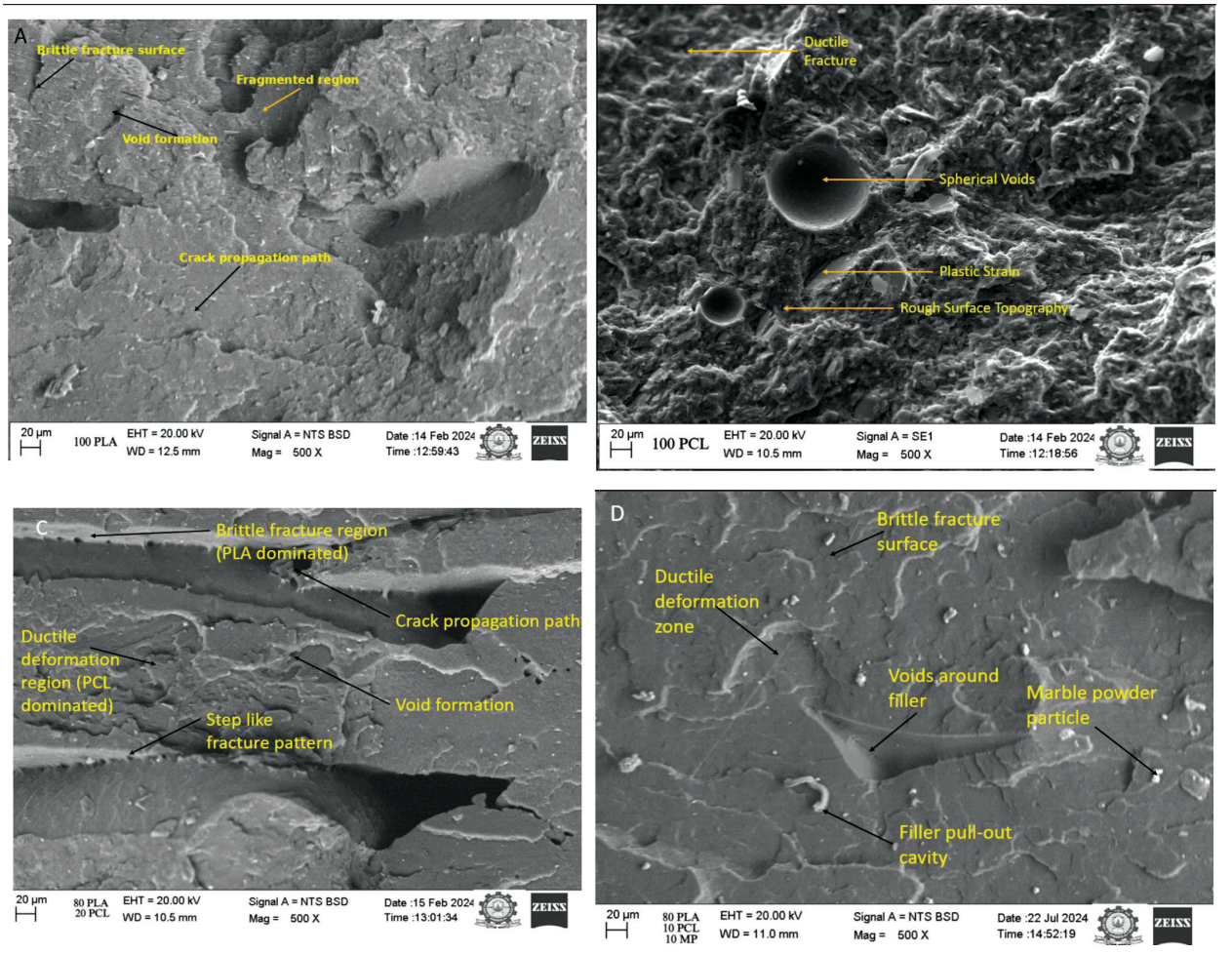

Figure 8: SEM images of impact-tested specimens

evant for demanding applications, including automotive components, where materials must withstand dynamic stresses while maintaining environmental sustainability.

Microstructural analysis of the fracture surfaces after impact testing provides important insights into the relationship between material composition and failure mechanisms. 100 % PLA exhibits a brittle fracture morphology, characterised by sharp and angular fracture features with minimal plastic deformation. This behaviour reflects limited energy absorption capacity and confirms PLA's rigidity and stiffness, but also its poor toughness. Such characteristics restrict its use in applications where resistance to dynamic loading is critical.

In contrast, 100 % PCL displays features typical of ductile failure, including extensive plastic deformation, rough fracture surfaces, and void formation. These features demonstrate the ability of PCL to absorb significant energy through stretching and necking before failure. This ductile nature makes PCL suitable for applications that demand toughness and flexibility but less so for load-bearing conditions where rigidity is essential.

The PLA/PCL (80/20) blend combines aspects of both brittle and ductile behaviour. PLA-dominated regions contribute stiffness, while PCL-rich regions enhance toughness through localised plastic deformation. However, void formation near phase boundaries indicates weak interfacial bonding and phase immiscibility, which limit stress transfer across the phases. Despite these limitations, the blend achieves a balance between rigidity and energy absorption, making it attractive for semi-rigid applications where both stiffness and toughness are required.

The influence of MP on the PLA/PCL system alters the fracture morphology by increasing stiffness but at the expense of toughness. MP acts as a rigid filler, contributing to structural reinforcement; however, poor dispersion and weak interfacial adhesion lead to voids, particle pull-out, and stress concentrators. These microstructural defects promote brittle fracture and limit the ductile contribution from PCL. As a result, although MP enhances stiffness, it reduces impact resistance, making such composites more suitable for applications where rigidity and dimensional stability are prioritised over toughness.

These findings highlight the importance of tailoring polymer blends and filler content to achieve targeted mechanical performance. PLA provides stiffness but lacks toughness, PCL contributes ductility and energy absorption, and MP enhances rigidity but introduces interfacial challenges. The balance of these effects underscores the need for strategies such as compatibilisation, improved filler dispersion, or surface modification of reinforcements to overcome phase immiscibility and interfacial weaknesses. These blends are essential for developing advanced biodegradable composites that meet application-specific requirements, particularly in fields such as packaging, biomedical devices, and automotive components.

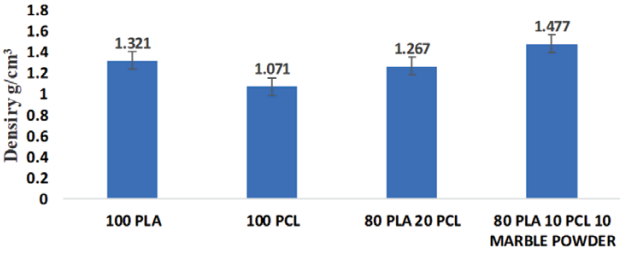

Figure 9: Results for the solid density of the composites

3.6 Solid density analysis

The densities of various composite materials were measured, including 100 % PLA, 100 % PCL, the 80 % PLA + 20 % PCL blend, and the 80 % PLA + 10 % PCL + 10 % MP composite. Pure PLA showed a density of 1.321 g/cm^3, while PCL had a lower density of 1.071 g/cm^3, reflecting its lighter inherent material properties. Incorporating 20 % PCL into PLA produced a blend with a density of 1.267 g/cm^3, falling between the values of the individual polymers, consistent with the rule of mixtures. Adding 10 % MP to this blend further increased the density significantly, reaching 1.477 g/cm^3. This increase is attributed to the higher density of MP (2.7 g/cm^3), which dominates the composite's overall density. Low standard deviations of all samples suggest consistent material preparation and measurement accuracy. These findings demonstrate that the density of PLA/PCL can be tailored by varying the blend ratio and introducing fillers like MP, making these composites adaptable for applications requiring specific density and mechanical properties. For instance, the increased density of PLA/PCL/MP composites can enhance stiffness and strength, which are critical for automotive and structural applications. Rifky Ismail et al.[33] observed that a bio-composite material composed of PLA40/PCL60/HA5 has the lowest density (1.09 g/cm^3), while a bio-composite material made of PLA85/PCL15/HA20 has the maximum density (1.45 g/cm^3). Within their theoretical and experimental density results, László Lendvai et al.[10] reported a narrow range of 1.24–1.39 g/cm^3. The PLA sample had the lowest density, while the PLA_20MD composite had the highest density, indicating a clear pattern of higher density at higher MD concentrations.

3.7 Comparison of mechanical properties between the proposed findings and other studies

The increased density of PLA/PCL/MP composites is due to the high density of MP (2.7 g/cm^3), influencing the overall composite density. Low standard deviations indicate consistent material preparation and measurement accuracy, making these composites suitable for applications requiring specific density and mechanical properties. Enhanced density improves stiffness and

Table 2: Comparison of mechanical properties between the proposed and existing materials

References	Sample	Impact strength KJ/m^2	Flexural strength MPa	Flexural modulus MPa	Tensile strength MPa	Tensile modulus MPa
[34] L. Lendvai et al.	Polyethylene terephthalate with 5% MP	15.5	< 92	2900	–	–
[3] A. Yadav et al.	70% PLA with 30% jute fibre	6.21	–	–	33.45	5340
[4] R. İncesu et al.	Tough PLA	–	–	1770	–	–
[5] M. Subramaniyan et al.	80% PLA-20% Al_2O_3	3	62	3500	30	650
[35] F. Sbardella et al.	PLA + basalt fibre	–	–	1700	–	–
[36] A. Fernández-Tena et al.	PLA 70 + PCL 30	0.08	–	2300	–	–
	PLA 30 + PCL 70	0.6	–	800	–	–
[10] L. Lendvai et al.	PLA + 5% MD	16.8	–	3500	–	–
	PLA + 10% MD	21.2	–	3830	–	–
	PLA + 15% MD	18.5	–	3980	–	–
	PLA + 20% MD	15.8	–	4390	–	–
Proposed materials	100 PLA	35.81	42.31	2410	19.3	539
	100 PCL	23.68	5.17	295	3.81	236
	80 PLA-20 PCL	30.1	60.03	3693	26.4	715
	80 PLA-10 PCL-10 MP	43.61	66.83	6220	36.76	1553

strength, crucial for automotive and structural applications.

PET + MP[34] showed moderate impact strength and flexural properties. PLA + jute fibre[3] improved tensile strength but lacked flexural data. Tough PLA[4] and PLA + basalt fiber[35] enhanced flexural modulus but lacked tensile data. PLA/PCL blends[36] had lower impact strength and modulus, particularly with the higher PCL content.

PLA40/PCL60/HA5 exhibited the lowest density (1.09 g/cm³), while PLA85/PCL15/HA20 had the highest density (1.45 g/cm^3)[33]. Theoretical and experimental density results for PLA + MD ranged from 1.24–1.39 g/cm^3, with increasing MD content correlating with higher density[11]. PLA + MD blends[10] showed increasing flexural modulus with higher MD content, ranging from 3500 MPa (5 % MD) to 4390 MPa (20 % MD).

The proposed 80PLA + 10PCL + 10MP blend achieved the highest impact strength (43.61 KJ/m^2) and flexural modulus (6220 MPa), surpassing previous findings. MP incorporation significantly enhanced rigidity, increasing tensile modulus (1553 MPa) and tensile strength (36.76 MPa), making this blend ideal for high-impact, stiff, and strong applications, particularly in the automotive industry.

4 CONCLUSION

The present study demonstrated that an addition of marble powder (MP), acting as the filler, to PLA/PCL blends significantly enhances the overall performance of the composites. The PLA/PCL blend itself exhibited improved flexural strength compared to 100 % PLA and PCL, indicating partial compatibility and synergistic behaviour between the two polymers. The addition of MP further reinforced the matrix, resulting in substantial improvements in flexural modulus and toughness, thereby reducing brittleness while enhancing structural stability. The XRD analysis confirmed an increase in crystallinity with the MP addition, which contributed to better load transfer and mechanical stability. Furthermore, SEM observations revealed that MP effectively refined the phase morphology, ensuring uniform dispersion within the matrix and reducing voids, which are often detrimental to mechanical performance. The density analysis indicated that MP, owing to its higher density, increased the overall density of the composite, thereby confirming its role as a rigid reinforcing filler. The combination of enhanced strength, improved toughness, and refined morphology demonstrates that PLA/PCL/MP composites exhibit superior mechanical integrity compared to 100 % PLA or PCL. Additionally, the utilisation of MP, an industrial by-product, not only improves material performance but also aligns with sustainability goals by promoting the use of eco-friendly polymers and reducing reliance on petroleum-based plastics. Overall, the findings confirm that PLA/PCL/MP composites offer a unique balance of strength, toughness, flexibility, and sustainability, making them promising candidates for lightweight and durable automotive components as well as other structural applications.

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